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FUEL CELLS FOR DIRECT TRANSFORMATION OF CHEMICAL ENERGY INTO ELECTRICAL ENERGY

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Many attempts have been made to convert the chemical energy of fuel directly into electrical energy without an intermediate conversion into heat. Various chemical reactions may be used to obtain electrical energy in a galvanic cell, if they are conducted so that exchange of ionic charge occurs. Electrochemists have long striven to obtain direct combustion of carbon or carbon monoxide by an electrochemical method.

In the opinion of Wilhelm Ostwald, the important problem concerning the best utilization of the chemical energy of fuel had to be solved by electrochemistry. In 1894, when Ostwald founded the Electrochemical Society, he asserted that the most important task of the society should be the replacement of the thermodynamical machine by the "chemicodynamical" machine. Shortly before this, Nernst had put forward his osmotic theory of the voltaic circuit, which made it possible to explain and calculate accurately electrode potentials in galvanic cells.

At the same time, chemical thermodynamics had shown the relationship between the emf of voltaic circuits and the equilibrium state of the chemical processes responsible for the emf, which made it possible to determine the interdependence of these two factors. In 1893, Nernst gave the corresponding numerical solution for the value of emf and amount of electrical energy in the reversible process of combining carbon and oxygen. The calculation showed that a thermodynamically reversible galvanic cell using carbon and oxygen has an emf of 1.02 volts at room temperature and has a conversion efficiency of 99.75%.

Thus, the direct conversion of the chemical energy of fuel into electrical energy is by no means a new problem. Many researchers have worked on it over a long period but most of this research has been fruitless. However,

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despite the great difficulties involved in the development of a fuel cell, researchers continue to work intensively on this problem; this is especially true in recent years, and at present some progress has been made, even if only under laboratory conditions.

Work in this field started comparatively recently in the USSR -- in the Institute imeni Karpov, in the laboratory of Academician V. N. Frumkin, and in the Power Engineering Institute imeni G. M. Krzhizhanovskiy of the Academy of Sciences USSR. The work done in the Power Engineering Institute forms the basis for this monograph.

The very successful results which we have obtained served as a stimulus for the publication of this monograph. These results represent a considerable step forward in this difficult field. The theoretical basis of the problem of fuel cells is set forth in the monograph. A thermodynamical calculation of the free energy and emf is given for various temperatures of the current-forming circuits: hydrogen-oxygen, carbon-oxygen I (before oxidation into CO), carbon-oxygen II (before oxidation into CO_2), and carbon monoxide-oxygen.

The efficiencies of fuel cells consisting of the above circuits at various temperatures are given from these calculations. The theoretical principles and thermodynamical calculations make it possible to appraise the problem of fuel cells and clarify possible methods of solving it.

The monograph includes a review of the historical development of fuel cells, in which the material having the most value from the scientific and historical standpoint was taken from periodical and patent literature, systematized, and evaluated.

A theoretical and experimental investigation of the chemical polarization of hydrogen and oxygen electrodes at room temperature made by the author at the Power Engineering Institute is described. This investigation revealed that the reason for the chemical polarization of hydrogen and oxygen electrodes was the slowness of the processes: (1) transfer of the atomic gas into the electrolyte solution in the form of ions (chemical polarization of the first kind); and (2) the adsorption of molecular gas on the surface of the electrode carrier and transition of the adsorbed gas from the molecular into the atomic state (chemical polarization of the second kind).

This theory was used to obtain an equation describing the chemical polarization of hydrogen and oxygen electrodes. This equation showed a linear dependency between electrode potentials and the logarithm of discharge current density. An experimental study of the chemical polarization of hydrogen and oxygen electrodes with different carrier-catalyzers confirmed the theory of chemical polarization of the hydrogen-oxygen cell.

On the basis of the study of chemical polarization of hydrogen and oxygen electrodes, series of substances with increasing polarizing properties were drawn up. These series agreed perfectly with the hydrogen and oxygen overvoltages in these substances and thus the theoretical proposition of parallelism between oxygen and hydrogen overvoltages in various substances and the ability of these substances to activate hydrogen and oxygen electrochemically was proven. On the basis of theoretical and experimental studies, we selected the best of the oxygen and hydrogen electrode carriers to construct a hydrogen-oxygen cell (or a hydrogen cell with air depolarization) for operation at room temperature. In these studies, it was found that hydrogenation catalysts are the best carriers for the hydrogen electrode.

A description is also given of a hydrogen cell with air depolarization and carriers of a mixture of silver sponge and activated carbon for the hydrogen electrode and a mixture of nickel sponge with activated carbon for the air electrode. The cell operated quite normally at room temperature with a sufficiently high discharge current density. Its efficiency was 60% at 25° C and a discharge current of one amp/sq dm and 56% at the same temperature and a discharge current of 2 amp/sq dm.

The cells of this type which we developed will permit the construction of a hydrogen-oxygen storage battery having very large capacity and prolonged charge storage.

One of the main parts of the monograph is the account of the author's work on the development of a high-temperature (500-900° C) gas cell with a solid electrolyte.

On the basis of literary data and his own experiments, the author selected the proper carriers for the carbon monoxide and hydrogen electrodes. The best carrier for the carbon monoxide and hydrogen electrodes was ferric oxide with a slight admixture of iron powder to increase the conductivity of the system; for the air electrode, the best carrier was a mixture of ferric oxide and magnetite. The most difficult problem in the development of gas cells with a solid electrolyte was that of finding solid electrolytes with the proper characteristics. In connection with this problem, the author made an extensive study and found many solid electrolytes which have high ionic conductivity and high chemical and temperature stability. In addition, other physicochemical properties of solid electrolytes, such as softening and melting points, ability to be formed, etc., were studied. Most of the solid electrolytes are easily obtained from combinations of sodium carbonate, Ural monazite sand, wolfram oxide, calcium oxide, quartz, etc. Many combinations of these sub tances are suitable for the solid electrolyte of a gas cell.

Of the various combinations of these substances, the following system proved to be best: 43% sodium carbonate, 27% Ural monazite sand, 20% wolfram trioxide, and 10% sodium silicate. This system had a resistivity of 10 ohm [-cm] at 550° and 1.2 ohm [-cm] at 900° C. It also has other properties required for the solid electrolyte of gas cells.

On the basis of these studies, a laboratory model of a carbon monoxide cell with air depolarization was designed and built. Tests of the cell revealed that it operated normally at temperatures from 550 to 900° C. The cell did not polarize at all. The internal voltage drop was directly proportional to the discharge current. The efficiency of the cell with respect to the heating effect of the chemical reaction was 58-62% at 700° C and a current density of 2-3 amp/sq dm [20-30 ma/sq cm].

The above makes it clear that considerable progress has been made toward the solution of the problem of fuel cells at room temperature, where the fuel source is hydrogen; and at high temperatures (550-900° C), where the fuel source is generator gas. Despite these accomplishments, however, the final formation of a fuel cell will require a good deal of time, just as was required for the final development of lead-acid and alkaline batteries.

In conclusion, we note that the problem of fuel cells, in which the chemical energy of fuel is converted directly and with high efficiency into electrical energy, is one of the most important and fascinating problems in contemporary science.

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